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SEQUENTIAL EXCITATION PREPARATION OF MOLECULAR ENERGY
LEVELS WITH SPECIAL (U) MASSACHUSETTS INST OF TECH
CAMBRIDGE DEPT OF CHEMISTRY R W FIELD ET AL. 31 DEC 87

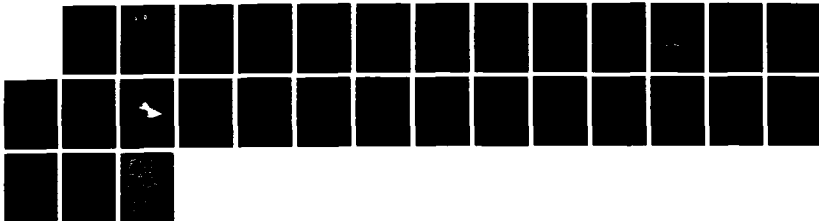
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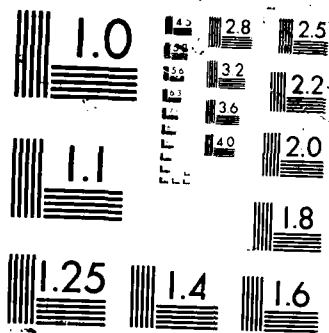
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19. ABSTRACT (Continue on reverse if necessary and identify by block number)

Our research accomplishments may be divided into the following ten areas:

1. Culmination of Stimulated Emission Pumping (SEP) Spectroscopic Studies of H₂CO.
Rotation-vibration assignments have been extended to levels of the H₂CO¹A₁ state at
energies as high as 11,500 cm⁻¹.2. Development and Testing of New Techniques. Two pulsed-cw schemes for monitoring
rotational energy transfer (RET) processes were devised and tested. One scheme relies on
transient absorption or gain (TA or TG) and the other on transient optical rotation (TOR).3. Collisional Properties of Highly Excited Vibrational Levels of H₂CO¹A₁. PUMP-
DUMP-PROBE studies of state-to-state RET at 11,400 cm⁻¹ reveal persistence of vibrational
identity, a-dipole propensity rules, and no dramatic increase in RET rates relative to
those in the zero point level.4. Collisional Properties of Rovibrational Levels of H₂CO¹A₂. RET studies in the
A¹ level with H₂CO, He, Ar, and N₂ collision partners reveal a-dipole propensity rules
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and persistence of alignment. In addition, we have shown that strongly J-dependent predissociation rates are the cause of the mysterious, highly nonlinear Stern-Volmer behavior of undispersed fluorescence subsequent to single rovibronic level excitation of $\text{H}_2\text{CO } \tilde{A}^1A_2$.

5. Dipole Moments in \tilde{A}^1A_2 H_2CO and D_2CO . Stark Quantum Beat Spectroscopic (SQBS) measurements on several vibrational levels (4^0 , 4^1 , 4^3) provide tests of a vibronic coupling explanation for the nonplanarity of the \tilde{A} state, a lower bound on the out of plane component of the electric dipole moment, and a sample of S_0 - S_1 vibronic interactions.

6. Studies of Chaos in Molecular Systems. A variety of statistical measurements of the quantum manifestations of classical chaos were applied to experimental and computed spectra of H_2CO .

7. Dipole Moments in \tilde{X}^1A_1 H_2CO . Stark effect measurements have been extended to higher vibrational levels than reported in J. Chem. Phys. 78, 3659 (1983) in order to test further the normal mode expansion of the molecular electronic dipole moment.

8. Rotational Reorientation in $\tilde{A}^1A_2\text{H}_2\text{CO}$. By selecting the polarization state of both PUMP and PROBE lasers, perfect $(J, K_a, K_c, M_J)_{\text{initial}}$ and $(J, K_a, K_c, M_J)_{\text{final}}$ selectivity is achieved. These experiments test predictions by Millard Alexander and the persistence of polarization deduced from our previous RET studies in the A and X states.

9. J-Dependent Quenching Rates in \tilde{A}^1A_2 D_2CO . Initial spectroscopic studies have identified the level schemes best suited to our planned Transient Gain measurements of J-specific collisional depopulation rates in \tilde{A}^1A_2 D_2CO . This study complements that in #4 above in that we expect the explanation for nonlinear Stern-Volmer behavior in D_2CO will be J-dependent quenching rates rather than J-dependent predissociation rates as in H_2CO .

10. Tunneling in Intramolecularly Hydrogen-Bonded Molecules. High resolution fluorescence excitation spectra of tropolone have been recorded and assigned. The observed tunneling doublings are apportioned between electronic excited and ground states, and the highly mode-specific effects on tunneling rates illustrate the profound effect of remote heavy atoms on large amplitude H-atom motions.

B. Research Objectives

1. Apply the Stimulated Emission Pumping (SEP) technique to highly excited vibrational levels of H_2CO and D_2CO .
2. Discover whether the rotation-vibration levels of $\text{H}_2\text{CO}/\text{D}_2\text{CO}$ remain well organized at chemically significant levels of vibrational excitation.
3. Develop new multiple resonance spectroscopic techniques capable of measuring rotational energy transfer rates (RET) in highly excited vibrational levels of H_2CO .
4. Develop statistical diagnostics for quantum ergodicity which are applicable to real SEP spectra of $\text{H}_2\text{CO}/\text{D}_2\text{CO}$ (Key word: ...)

C. Status of Research Effort

Significant progress toward all of the cited objectives has been made. It is expected that our research emphasis will shift from studies of $\text{H}_2\text{CO}/\text{D}_2\text{CO}$ to new experiments on HCN/DCN , $\text{NH}_2^+ + \text{O}_2$, and tropolone during the first year of the new grant, AFOSR-88-0062.

Technical Progress Report 1 October 1984 - 31 October 1987

By the start of the current contract/grant, Stimulated Emission Pumping (SEP) had become a fully-developed technique, which had seen many applications. A few remaining details of the developmental stage and some spectroscopic applications of SEP were cleaned up near the start of the current grant. The stage was then set to address new techniques needed to progress into studies of the collisional properties of highly energized molecules. These techniques and the beginnings of their applications constituted the main effort of the past three years. The following ten sections summarize the major accomplishments.

1. Culmination of Early SEP Studies (P.H. Vaccaro, H.-L. Dai, and C. Korpa)

The earliest phase of work supported by the current contract/grant brought to a close the developmental stage of Stimulated Emission Pumping

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(SEP) as a spectroscopic technique. The high resolution and J, K_a selectivity of SEP opened the possibility for study of individual rovibrational levels in the ground electronic state with unprecedentedly high amounts of vibrational energy. Several properties of levels at such "chemically interesting" energies have been discussed in the literature. Among these are intramolecular vibrational randomization (IVR), chaotic behavior of classical trajectories and spectroscopic evidence for ergodicity.

A large set of rovibrational levels of $\text{H}_2\text{CO } \tilde{X}^1\text{A}_1$ was investigated by SEP in the energy range $7400 \text{ cm}^{-1} < E_{\text{vib}} < 8600 \text{ cm}^{-1}$. For low values of the rotational quantum numbers J and K_a ($J < 3$, $K_a < 1$), the spectra were simple and each observed level could be assigned a set of normal mode quantum numbers. As J was increased, features associated at low J with a single vibrational basis function were observed to divide their intensity among an increasing number of closely spaced transitions. At $J \approx 10$, $K_a \approx 2$ the number of observed levels exceeds that calculated from the known purely vibrational density of states, ρ_v . It did not, however, reach as high as $(2J + 1)\rho_v/4$, the total density of rovibrational levels of a given symmetry species [1,2]. This strongly rotation-induced IVR was substantiated by a plausible Coriolis-coupling model for H_2CO [2]. Use of a "fraction of phase space" parameter proposed by Stechel and Heller showed that the motion becomes less rather than more ergodic with increasing J if the "accessible" phase space is defined as including all $K_a < J$ values [1].

Another effort carried over from the previous contract involved state-specific rates of the $\text{H}_2\text{CO}(S_0) \rightarrow \text{H}_2 + \text{CO}$ unimolecular decomposition [3]. Specific \tilde{A} -state (S_1) rovibrational levels in the 28000 cm^{-1} region of energy were differentially Stark tuned in energy relative to a dense



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manifold of background S_0 levels by application of a static electric field, a technique that had been introduced earlier by Weisshaar and Moore [4]. Three sets of measurements were made as a function of field strength: (i) Integrated fluorescence within a 1 μ s gate, (ii) fluorescence decay curves, (iii) quantum beat frequencies (for measurements with the field perpendicular to the laser polarization). In the neighborhood of "anticrossings", all three quantities exhibit anomalies which can be analyzed in terms of a simple two level model with each zeroth order level having an imaginary energy component to account phenomenologically for its intrinsic decay rate. The upshot was that two S_1 levels, both having $J = 2$ and of the same rovibrational symmetry and only 30 cm^{-1} apart in energy interacted with S_0 levels whose unimolecular decay rates (corresponding to $\text{H}_2\text{CO} \rightarrow \text{H}_2 + \text{CO}$) differed by a factor of 2.5. Moreover, contrary to naive expectations, the higher energy level exhibited the slower dissociation rate. The number of levels investigated by this technique was insufficient to produce an estimate of the height of the barrier to dissociation.

At this point, the stage was set to move on to applications of SEP to the study of collisional properties of highly energized molecules and to other new endeavors.

2. Development and Testing of New Techniques (P.H. Vaccaro and F. Temps)

Once the spectroscopic capabilities of SEP had been thoroughly established, interest turned to collisional transfers either among neighboring levels of the \bar{A} -state (denoted as $|a\rangle$) or among highly excited vibrational levels in the \bar{X} state (denoted as $|x^\dagger\rangle$). Methods were needed to monitor the small populations likely to be present at a given time in any specific $|x^\dagger\rangle$ or $|a\rangle$ of interest. Noise introduced into the average signal by shot-to-shot

instabilities in the intensity of both PUMP and DUMP pulsed lasers was also problematic. Accordingly, a method was sought that was both highly sensitive and relatively noise free.

Two basic schemes were investigated and characterized, one relying on transient absorption or gain (TA or TG) and the other on transient optical rotation (TOR). Both schemes employ a single-mode cw PROBE laser. For the purpose of discussion, assume an $|x^\dagger\rangle$ level is to be monitored. The PROBE laser would be tuned to the frequency of a specific $\tilde{A} \leftarrow \tilde{X}$ transition originating in the $|x^\dagger\rangle$ of interest.

In the absence of an SEP sequence of PUMP/DUMP pulses, there will be no population in $|x^\dagger\rangle$ and the PROBE laser will be transmitted without attenuation. When $|x^\dagger\rangle$ become populated as the result of SEP, either directly or through collisional transfer, some of the PROBE will be absorbed. The magnitude of this absorption at a given time gives rise to a TA signal that reflects the population of $|x^\dagger\rangle$ at that time. To monitor the population of an $|a\rangle$ level, this scheme is inverted. The PROBE laser transition has as its upper level the $|a\rangle$ of interest and as its lower level any convenient $|x^\dagger\rangle$ (generally not a highly excited $|x^\dagger\rangle$, but necessarily one with negligible thermal population). In this case the signal appears as gain rather than absorption. The initial TG measurements used a single-mode Argon ion laser as the PROBE laser because of the unique amplitude stability of such devices. This limited the choice of $|a\rangle$ levels that could be probed to those with $\tilde{A} \leftarrow \tilde{X}$ transitions coinciding in frequency with one of the Argon ion laser lines. Later, however, a differential detection scheme was devised that permitted using as the PROBE a tunable cw single mode laser, in spite of the relatively large amplitude noise of such a laser. A

"reference" intensity was obtained by splitting off a small fraction of the PROBE beam just before it entered the sample cell. The "signal" intensity was taken as the PROBE laser intensity after passage through the cell. A differential signal-minus-reference amplifier was adjusted to give a null reading in the absence of SEP pulses.

The second method (TOR) employs a polarized PROBE beam with a crossed polarizer in front of the detector to block the PROBE beams. When there is a population in the $|x^{\dagger}\rangle$ or $|a\rangle$ being probed, this population will be nonuniformly distributed over the M_J sublevels. This gives slightly different absorption (or gain) between right-and left-circularly polarized PROBE radiation, which in turn produces a slight optical rotation of the PROBE beam, allowing some of it to reach the detector. TOR is a "zero-background" technique; i.e., when the level of interest is empty there is no signal.

Both TG/TA and TOR have now been developed to a useable stage for probing either $|x^{\dagger}\rangle$ or $|a\rangle$ type levels. In state-to-state measurements, the two techniques give independent measures of the temporal development of population in a level populated through collisional transfer from the initially prepared level. However, for measurement of the decay rate of the initial level, the two techniques provide different information. TG or TA is sensitive only to collisions that affect inelastic transfer to levels of a different energy. In TOR, however, collisions also "count" which only affect the distribution among M_J sublevels of the initially prepared level (elastic reorientation). Thus, combination of the two methods allows an assessment of the relative importance of $\Delta M_J = 0$ collisions and $\Delta M_J \neq 0$ collisions.

3 . Collisional Properties of Highly Excited Vibrational Levels of H₂CO

\tilde{X}^1A_1 (F. Temps, P.H. Vaccaro, S. Halle)

The development of sensitive probe techniques opened the way to use SEP as a preparative method for studying the effects of gas phase collisions on molecules in any one of the wide variety of \tilde{X} -state rovibrational levels. Some fundamental questions that could then be addressed included: (1) How does the total depopulation rate of a level depend on the density of nearby vibrational levels?, (2) Are there significant differences in the collisional properties of different levels?, (3) After a collision, does a molecule "remember" its initial vibrational identity or does it behave statistically?

The temporal evolution of populations in initially prepared levels as well as collisionally populated levels has been investigated as a function of scattering gas pressure for highly vibrationally excited H₂CO with ~ 11500 cm⁻¹ of vibrational energy in the ground electronic state \tilde{X}^1A_1 . At this energy the mean spacing between adjacent vibrational levels is ~ 2.5 cm⁻¹. This is to be compared to the rotational constant $\frac{B+C}{2} \sim 1.2$ cm⁻¹. Hence, for modest values of J there will be several same-J, K_a vibrational levels closer to a prepared level than the nearest rotational level for the same vibrational state. The state prepared by SEP has been assigned as 2₄4₄.

The rate constants for overall depopulation of several rotational levels of H₂CO (\tilde{X}^1A_1 , 2₄4₄) in collision with H₂CO at room temperature were found to be $k \sim 1.8 \times 10^{15}$ cm³ mol⁻¹s⁻¹, with no systematic dependence on initial J or K_a values for unperturbed $|x^\dagger\rangle$ levels. This exceeds the gas kinetic Lennard-Jones collision rate by about one order of magnitude. The

equivalent cross section is $\sigma \approx 500\text{\AA}^2$. For levels known to be strongly coupled to other vibrational levels via Fermi or Coriolis interaction the overall decay rates were found to increase by as much as 40%. Rate constants for collisional energy transfer with He were found to be $k \approx 2.2 \times 10^{14} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, corresponding to $\sigma \approx 28\text{\AA}^2$.

An analysis of state-to-state measurements (see Fig. 1) for $\text{H}_2\text{CO}-\text{H}_2\text{CO}$ collisions, based on a simplified master equation approach, revealed the dominance of rotational energy transfer with $\Delta K_a = 0$ and $\Delta J = \pm 1$. These transitions, predicted to dominate for scattering governed mainly by dipole-dipole interactions, have $k_{\pm 1} \approx 4.6 \times 10^{14} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. The $\Delta J = \pm 2$ collisions have $k_{\pm 2} \approx 0.9 \times 10^{14} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, and $\Delta J = \pm 3$ collisions give $k_{\pm 3} \approx 0.4 \times 10^{14} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. A more refined master equation analysis is in progress, but it is not expected that the general conclusions will be significantly modified. Apparently, in H_2CO at $E_{\text{vib}} \approx 11500 \text{ cm}^{-1}$ purely rotational energy transfer with conservation of vibrational motion dominates at least as long as the initial level is not strongly perturbed. Measured J-changing, vibration-preserving rates sum to 80% of the total depopulation rate of the initial level. This is not a wholly surprising result because the vibrational levels in this region still seem to be regular (as opposed to chaotic) by other criteria. These results, however, do provide the first evidence for persistence of vibrational identity in a system where the energy gap for vibrational energy transfer is comparable to or smaller than that for rotational energy transfer. An important next step will be to push these investigations to higher energies and/or higher initial J, K_a values where the level structure suggests chaotic vibrational motion.

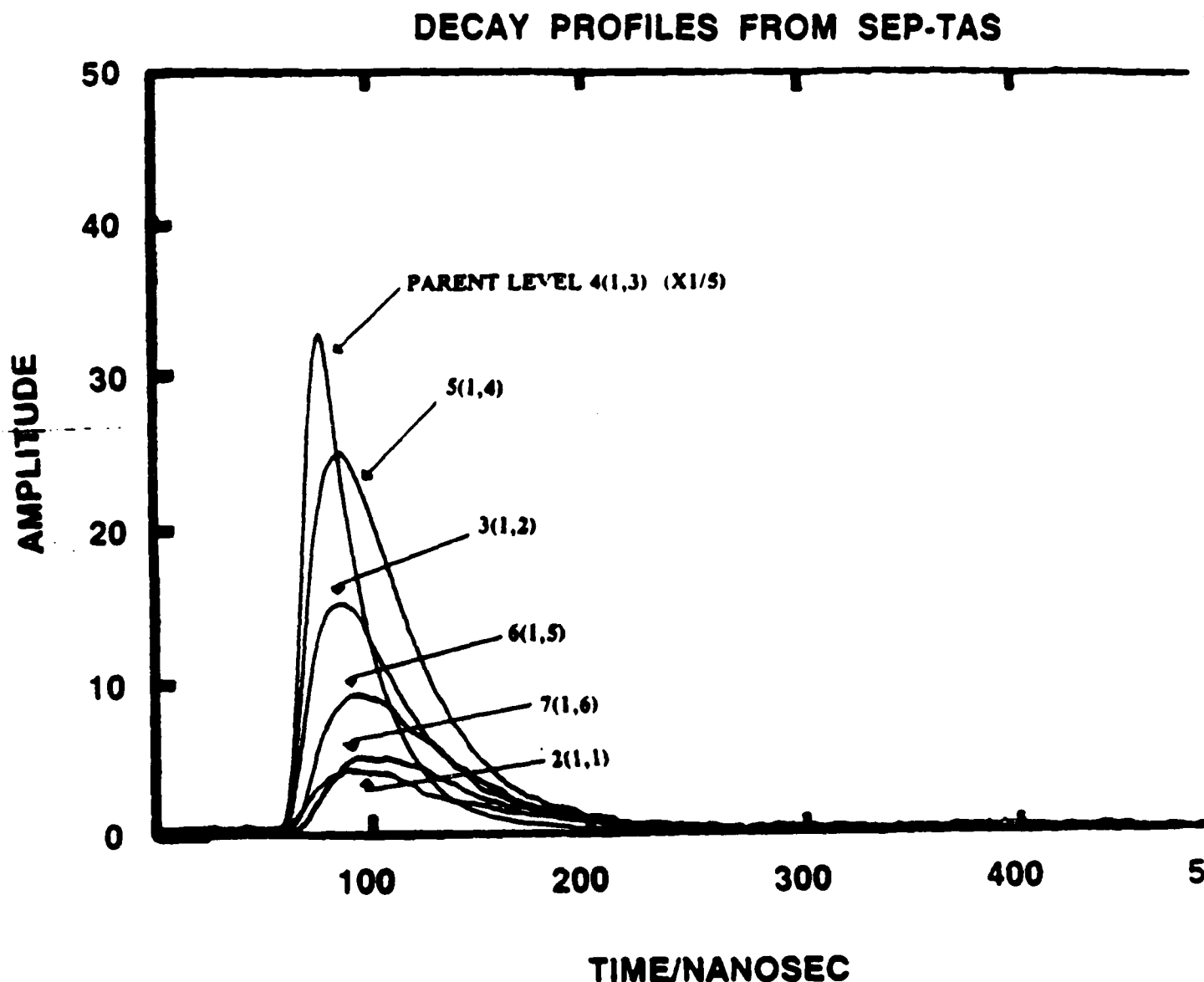


Figure 1. Transient populations of individual J-levels in the $\text{H}_2\text{CO } X \ 2_{44} \ K_a = 1$ vibrational level (near $11,500 \text{ cm}^{-1}$) monitored by SEP-TA. The PUMP/DUMP process populates the $J_{K_a, K_c} = 4_{1,3}$ level. The $4_{1,3}$ level population is shown attenuated by a factor of 5 relative to those of the $2_{1,1}$, $3_{1,2}$, $5_{1,4}$, $6_{1,5}$, and $7_{1,6}$ levels. Note that the SEP-TA measurements show that the signals from the collisionally populated levels rise after the signal from the SEP-populated initial level begins to fall, and the population maxima in the collisionally populated levels are of decreasing magnitude and increasing delay as $|\Delta J|$ increases.

Most of the \tilde{X} -state measurements relied on transient absorption. A few depopulation measurements were made using transient optical rotation, and they gave essentially identical rate coefficients. This shows that there is very little reorientation of rotational angular momentum when $\Delta J = \Delta K_a = \Delta K_c = 0$ (elastic reorientation accounts for <5% of the total depolarization rate). Future studies employing both methods for state-to-state and pure depopulation processes should shed further light on propensity rules for ΔM_J for various possible $\Delta J, \Delta K_a$.

4. Collisional Properties of Rovibrational Levels of $H_2CO \tilde{A}^1A_2$

(P.H. Vaccaro, F. Temps)

Measurements very similar to those described above were also carried out for $H_2CO \tilde{A}^1A_2$ rotational levels [5]. Both the TG and the TOR techniques were used. State-to-state rates were measured for H_2CO self-relaxation and for He, Ar and N_2 as collision partners. The $\Delta K_a = 0$, $\Delta J = \pm 1$ a-dipole processes were found to be the most important. However, direct $\Delta J = \pm 2$ collisional transitions as well as fluorescence quenching (probably via $H_2CO \rightarrow H_2 + CO$) were found to account for a significant fraction of the total depopulation rate. N_2 as a collision partner gave a larger ratio for $\sigma(\Delta J = \pm 2)$ to $\sigma(\Delta J = \pm 1)$ than did atomic collision partners. This suggests that the permanent quadrupole moment of N_2 ($Q = 0$ for atoms) is comparable in importance to the induced dipole in causing rotational relaxation in H_2CO . As in the case of high vibrational levels of the \tilde{X} -state, collisions seem to be dominated by small values of ΔM_J , at least as far as $\Delta J = \Delta K_a = \Delta K_c = 0$ processes are concerned.

5. Dipole Moments in \tilde{A}^1A_2 Formaldehyde (P.H. Vaccaro)

The dependence of electronic structure on vibrational and rotational degrees of freedom has long been a subject of interest and controversy in molecular physics. Substantial effort has been directed towards the measurement of electric dipole moments as a function of rotational and vibrational quantum numbers. Among the techniques that have been used are microwave Stark spectroscopy, molecular beam electric resonance, microwave-infrared double resonance and laser Stark spectroscopy. In contrast to the wide scope of measurements on ground electronic states, very little information exists for dipole moments of electronically excited states of polyatomic molecules. This is principally because of the stringent requirements for resolution and sensitivity, which are very difficult to achieve using traditional optical methods. For a moderate-size molecule such as formaldehyde, whose lowest energy electronic transition occurs at $\sim 28,000 \text{ cm}^{-1}$, the spectral shifts produced by reasonable electric field strengths are at most on the order of a few tenths of a cm^{-1} . In gas samples, the accuracy with which these small splittings can be directly observed is limited by Doppler broadening, which is typically $>0.1 \text{ cm}^{-1}$ at room temperature. Consequently, Stark effect measurements on excited electronic states are problematic and seldom yield molecular dipole moments of high accuracy.

Stark Quantum Beat Spectroscopy (SQBS) is a technique we have developed to get around these limitations. In the optical excitation of a molecule in a static electric field, the selection rule $\Delta M_J = \pm 1$ holds when the exciting radiation is polarized with its polarization vector perpendicular to the static field. This leads to the preparation of a coherent superposition of levels with M_J differing by ± 2 , provided that the coherence linewidth of the exciting laser is broad enough to span the difference in energy between the

two sublevels differing in M_J by ± 2 . For example, excitation to a $J' = 2$ state would prepare a coherent superposition of $M_J' = 2$ and $M_J' = 0$ since both M_J -components can be reached from $M_J'' = 1$. Following the initial preparation, this non-stationary state will evolve in time, with a recurrence of the initial coherence at $t \cdot \Delta\nu = 1$ where $\Delta\nu$ is the splitting (in frequency units) between, say, $M_J = 2$ and $M_J = 0$. Different M_J states radiate with different polarization characteristics. Hence, there are polarization-dependent detection arrangements that exhibit the periodic evolution of the prepared non-stationary state in the form of sinusoidal modulation of the fluorescence. The frequency of this modulation is $\Delta\nu$. Figure 2 shows the modulated fluorescent decay from the $2_{1,1}$ rotational level of $\text{H}_2\text{CO } \tilde{\text{A}}^1\text{A}_2^1$. Fourier analysis of the oscillatory part of the intensity yields a high precision value of the Stark splitting. The quantum beat frequencies are essentially free of Doppler broadening since the two coherently excited transitions are in the same molecule, which has some characteristic velocity v . Stark splittings with frequencies up to ~ 100 MHz can be resolved and measured to high precision (~ 1 part in 10^4) using this technique. For a 100 MHz Stark splitting, the residual Doppler broadening is of the order 200 Hz and completely negligible relative to homogeneous broadening.

SQBS permits determinations of molecular dipole moments of electronically excited molecules to a precision better than 0.001 D. This is higher precision than had been thought possible or previously achieved. The high precision Stark coefficients that were determined for various rovibrational levels of the $\text{H}_2\text{CO } \tilde{\text{A}}$ -state provide a convenient secondary standard for electric field strengths. H_2CO is a gas at room temperature. It can easily be introduced into any Stark cell for calibration by

observation of the quantum beat frequencies for a given rovibrational transition.

From a scientific point of view, the Stark effect of \tilde{A} -state H_2CO is interesting as a check on ab initio electronic structure calculations, as a probe of local S_0 - S_1 perturbations, and as a check on a "vibronic coupling" model put forward by Innes [105]. The equilibrium geometry in the \tilde{A} -state has a significant bending angle between the CO bond and the HCH plane. For such configurations, the molecule can have components of the dipole moment both along the molecular a-axis (roughly parallel to the CO bond) and along the c-axis (roughly the "out-of-plane" direction). Stark coefficients are sensitive to both components, although the much less so for μ_c than μ_a ; μ_c survives vibrational averaging only as a transition moment between inversion-doublet vibrational states (e.g. 4^0 and 4^1 states). At the present state of data analysis, which is incomplete, it is possible to set a limit on the possible size of μ_c which is close to the ab initio prediction of that quantity.

For a given vibrational state, the Born-Oppenheimer approximation predicts a simple and smooth variation of dipole moment with rotational state. The observed differences among the five $J = 2$ rotational levels of 4^1 \tilde{A} -state H_2CO do not follow such a simple pattern and probably owe to weak non-adiabatic S_1 - S_0 interactions.

Finally, the Innes vibronic coupling model [6] makes definite predictions about the variation of the dipole moment with ν_4 (the out-of-plane bending vibration) in terms of the dipole moments of the two unperturbed electronic states (\tilde{A} and \tilde{B}) that are coupled through the ν_4 vibration. This model

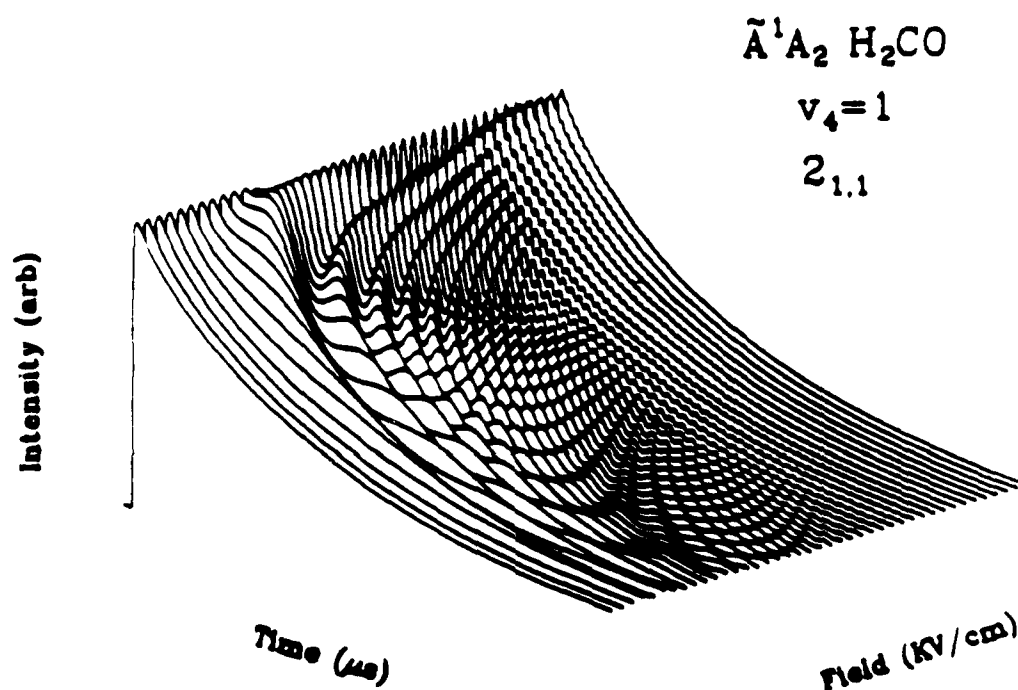


Figure 2. A perspective view of quantum beats in the $2_{1,1}$, $v_4 = 1$ rovibrational level of A^1A_2 formaldehyde. The axes display three experimental parameters: normalized spontaneous emission intensity (arbitrary units), time (ranging from 0 to 2 μ s), and electric field strength (ranging from 0 to 3.1 kV/cm).

succeeded remarkably well in fitting the observed ν_4 vibrational spacings of H_2CO , D_2CO and HDCO . It failed, however, to predict the observed trends with ν_4 of the dipole moments of H_2CO and D_2CO , at least when ab initio values of $\mu(\tilde{A})$ and $\mu(\tilde{B})$ are used. Further analysis of the ν_4 dependence is in progress.

6. Studies of Chaos in Molecular Systems (S. Halle, R. Jost, J.P. Pique)

One of the successes of SEP has been to provide experimental data on real molecules in an energy regime where it is likely that the corresponding classical systems would exhibit chaotic motion. Several criteria have been developed for extracting information from spectra about the extent and rate of unimolecular intramolecular vibrational randomization (IVR). These methods all rely on analyses of the statistical properties of dense spectra. Most of this work has relied on acetylene SEP spectra, and was not AFOSR supported. However, some specific applications were made to H_2CO spectra, and a number of computational efforts related to the AFOSR project are under way. Much of the theoretical work is being undertaken in collaboration with theorists at other institutions. Principal among these so far is a collaboration with the group of Maurice Lombardi, Remy Jost and Jean-Paul Pique at Grenoble. Two graduate students (Peter Green and Scott Halle) from the M.I.T. group have spent several months in Grenoble, and Dr. Pique just completed a year's stay at M.I.T. Besides the Grenoble connection, collaborations are starting with R. Wyatt and R. Friesner at Texas, with M. Kellman at Northeastern and R.D. Levine at Hebrew University. Each of these collaborations brings a different point of view to the analysis of SEP spectra.

R. Jost (Grenoble) has done an extensive numerical study aimed at discovering what kinds of interactions are required to convert a spectrum from one indicating regular dynamics into one indicating chaotic dynamics. He starts with a diagonal matrix whose matrix elements are randomly placed with

respect to each other in some range. Off-diagonal matrix elements are then added in a variety of ways, the complete matrix is diagonalized and statistical properties of the resulting spectrum are analyzed. Specifically, Jost examines the "Brody parameter" [7], an indicator of the distribution in spacing between nearest neighbor eigenvalues. Jost was able to show that almost any distribution of the off-diagonal matrix elements would lead to the same Brody parameter for the same average size of the off-diagonal element, provided that the matrix was not too sparse.

S. Halle of the M.I.T. group, in collaboration with Jost, has extended this work using a reasonable model for H_2CO . Halle generated diagonal matrix elements from a Dunham-type expansion, using experimentally determined parameters fitted to a large set of lower-lying eigenvalues. To this he added plausible off-diagonal matrix elements for coupling between the various zeroth order states. This H_2CO -based calculation produced the same conclusions as Jost's earlier work, namely, that the Brody parameter provides a measure of the average coupling matrix element in the best possible anharmonic oscillator product basis set.

In another collaboration, with R. Wyatt and R. Friesner, extensive calculations using their RRGm technique [8] are being undertaken for the HCN molecule, a target for future experimental SEP study. These calculations use the best complete \bar{A} and \bar{X} state potential energy surfaces available for HCN. The RRGm methods allows accurate calculation of SEP transition intensities from a given \bar{A} -state rotation-vibration level, without any computational restrictions on J' , K_a' , or l'' . These predicted transition strengths and level spacing patterns will provide insights into the dynamical interpretation and spectroscopic assignment of SEP spectra, even if the model for the \bar{X} -state

potential is inaccurate at the high energies expected to be sampled by SEP spectra. The computed SEP spectra will tell us what to look for, what resolution and dynamic range will be required, what the spectrum of H orbiting CN will look like, and how the spectral chaos measures will change when the classical dynamics changes from quasiperiodic to chaotic. As this work progresses, it is expected that a strong theory/experiment interplay will focus and redirect the course of action for both experiment and theory.

7. Dipole Moments in \tilde{X}^1A_1 H₂CO (S. Halle, S. Taddy)

Vaccaro et al [9] showed that the electric dipole moment in the \tilde{X} state of H₂CO could be expressed as a Dunham type polynomial

$$\mu_v = \mu^0 + \sum_i \mu_i v_i + \sum_{i>j} \mu_{ij} v_i v_j$$

for levels involving overtones and combinations of modes 2 and 4 up to a total energy of 6400 cm⁻¹. Using the same technique, SEP-Stark spectroscopy, Halle and Taddy measured dipole moments for several vibrational levels at

$E > 6400$ cm⁻¹ and for combination levels involving modes in addition to 2 and

4. The purpose of his work was to discover whether μ exhibits the increasingly pervasive mode mixing at high E in the same way as the vibrational energy levels and $\tilde{X} \rightarrow \tilde{X}$ transition intensities. The results of the new SEP-Stark experiments are being analyzed by Mr. Halle.

8. Rotational Reorientation in \tilde{X}^1A_2 H₂CO (S. Halle, S. Coy)

Using a linearly or circularly polarized PUMP, a single M_J -component of a 0_{00} , 1_{01} , 1_{10} , or 1_{11} rotational level of the H₂CO \tilde{X} -state can be populated. With a linearly or circularly polarized PROBE, populations may be measured for each M_J -component of all $J \geq 1$ and some $J=2$ rotational levels. This OODR scheme

is similar to that used by Silvers et al. [10] to study single collision depolarization in $\text{BaO } A^1\Sigma^+$. There is the added complexity here that the depolarization accompanying collision induced transitions across the $l_{10} + l_{11}$ asymmetry doublet can be monitored. Propensity rules proposed by Alexander et al. [11] will be tested experimentally. The agreement between rate coefficients for rotation changing collisions inferred from Transient Gain/Absorption and Transient Polarization spectroscopies [5,12,13] implies remarkable persistence of orientation and alignment in rotationally inelastic collisions. The $l_{10} + l_{11}$ asymmetry doublet transition is of particular significance because the M_J -selection rules for electric dipole $\Delta J=0$ transitions are qualitatively different from those for $\Delta J = \pm 1$ transitions. Furthermore, this is the only $\Delta J=0$ transition expected to have sufficient dipole intensity to be observable in our experiments. S. Halle and S. Coy have performed initial M_J -selective SEP-RET studies.

9. J-Dependent Quenching Rates in \tilde{A}^1A_2 D_2CO (S. Halle).

Vaccaro et al. [13] have shown that the explanation for the nonlinear Stern-Volmer behavior of $\text{H}_2\text{CO } \tilde{A} v_4=1$ is rapid RET combined with enormous J-dependent variations in predissociation rate [14]. This unimolecular mechanism cannot explain similar Stern-Volmer nonlinearities in D_2CO because the predissociation contributions to the single rovibronic level lifetimes in $v_4=1$ have been shown to be negligible [14].

S. Halle is ready to begin measuring total collisional depopulation rates for individual $J_K a_K c$ levels of $\text{D}_2\text{CO } \tilde{A} v_4=1$ by Transient Gain and Polarization spectroscopies. Using a collision partner (eg He) which is minimally effective in causing rotationally inelastic collisions, we expect to see

significant variations in the depopulation rates which are associated with quenching ($\tilde{A} \text{ D}_2\text{CO} \rightarrow \text{D}_2 + \text{CO}$) rather than RET.

10. Tunneling in Intramolecularly Hydrogen-Bonded Molecules (R. Redington, Y. Chen, G. Scherer, and M. Hunter)

The fluorescence excitation spectrum of the $\tilde{A}^1\text{B}_2\text{-}\tilde{X}^1\text{A}_1$ system of tropolone, cooled by supersonic jet expansion, has been recorded and assigned [15]. Tunneling doublets, associated with an internally hydrogen bonded H-atom transferring between two O atoms, have been resolved and interpreted. This work provides decisive examples of mode-specific tunneling. Small motions of heavy atoms remote from the light atom tunneling site, are shown to have enormous effects on the tunneling rates.

This work is being done by Professor R. Redington who is a frequent visitor to MIT from Texas Tech University. He has installed a supersonic jet apparatus in our SEP laboratory at MIT and, with Martin Hunter, has extended his study of tropolone to other isotopomers. We hope to use this apparatus to perform SEP spectroscopy on tropolone as well as other internally H-bonded molecules.

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Dr. Hai-Lung Dai (H_2CO SEP)
Dr. Charles Hamilton (HCN)
Dr. Jean-Paul Pique (Quantum Ergodicity)
Dr. Friedrich Temps (H_2CO , TPS, TAPS)

3. Graduate Students

Scott Halle (H_2CO and D_2CO SEP, Quantum Ergodicity, Stark Effect, TGS and TPS)
David Jonas (Quantum Ergodicity, HCN)
James Lundberg ($\text{NH}_2^\dagger + \text{O}_2$)
Patrick Vaccaro (H_2CO TGS, TPS, TAPS)

4. Undergraduate Students

Martin Hunter (Deconvolution of Transients, tropolone)
Stephanie Taddy (H_2CO Stark Effect)
Ann Zabludoff (H_2CO , D_2CO Stark Quantum Beats)

F. Interactions: Spoken Papers (since 1984)

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 - 30a. "The Evolution from Trivially Assignable to Intrinsically Unassignable Spectra: From RKR to RRKM,".
 - 30b. "Quantum Ergodicity: Time Scales, What is Accessable?, and Collisions,".
 - 30c. "Stark and Zeeman Quantum Beat Spectroscopy of Formaldehyde and Acetylene,".
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43. R.W. Field, "Acetylene: Isomerization, Dissociation, and Chaos", University of Washington, Department of Chemistry (October 14, 1987).
44. R.W. Field, "Acetylene: Dissociation, Isomerization, and Quantum Chaos", Chemistry Division, Oak Ridge National Laboratory (October 23, 1987).

G. Patents

None.

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